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Metal-rich metallaboranes constitute practical, low temperature precursors for the vapor deposition of pure, amorphous alloy thin films. This has been demonstrated for the compositions Fe_4B and Fe_3B. Further, the same approach permits the deposition of refractory borides, e.g., MnB_4, under mild conditions. Reaction observed during deposition suggests a route to ternary films of precise composition. The results also suggest that main group-transition element clusters in general constitute sources of solid state materials with compositions fixed by the precursor.

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METALLABORANES AS PRECURSORS TO METALLIC GLASSES

FINAL REPORT

Thomas P. Fehlner

December 9, 1989

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1. FOREWORD

The properties of metal alloys in the amorphous state are of great interest. We have demonstrated that metal-rich main group atom clusters constitute practical, low temperature precursors for the production of pure amorphous (glassy) metal films. Further, we now know that controlled reaction during deposition, e.g., oxidation, also has promise for the production of ternary films with precisely controlled composition. In addition, we have demonstrated that a boron-rich metallaborane is a low temperature precursor for a refractory boride film. This suggests that the pyrolysis of an appropriate metallaborane is an attractive route for the deposition of uniform, pure, thin coatings of metal borides on a variety of substrates.

2. REPORT

A. STATEMENT OF THE PROBLEM:

Metal organic chemical vapor deposition (MOCVD) is a well established, practical technique for forming simple as well as complex solid state films[1]. For binary systems the conventional approach is to use mixtures of the most readily available molecules containing the elements of interest. This approach often is complicated by the problems of handling high pressure, toxic gases, complete mixing of the reagents and disposal of excess precursor. In addition the molecules used are usually difficult to activate and require rigorous conditions for deposition. This leads to restrictions in the types of substrates that can be utilized and, in the case of thermal deposition, often only results in the formation of the most stable form of the solid.

In recent years a number of groups have developed compounds that serve as single precursors for specific binary materials[3,4,5,6,7,8,9,10,11,12] In such an approach, the objective is to synthesize precursor molecules that are easy to handle, that have low toxicity, and which contain a low energy decomposition pathway to a material of desired stoichiometry. When successful these rational precursors have the desired properties of convenience and safety. As importantly, they create opportunities for preparing films of presently known stoichiometry with new properties as well as for exploring systems of unknown stoichiometry and properties.

During the past three years we have demonstrated that metallaboranes and closely related cluster compounds serve as precursors to alloy thin films under relatively mild

conditions. Under the proper conditions the stoichiometry of the material is determined by that of the cluster. Some of the materials synthesized exhibit the properties of known amorphous metal borides while others exemplify routes to presently unstudied materials. The work establishes metallaboranes in general as practical molecular precursors to transition metal boride films of varied stoichiometry and elemental composition. The following delineates in more detail these findings and outlines proposals for future exploitation.

B. SUMMARY OF MOST IMPORTANT RESULTS:

1. Glassy Iron-Boron Films: The major objective of our original proposal was to demonstrate that metal-rich ferraboranes constitute useful precursors for the deposition of thin metal-metalloid films under mild conditions with precisely controlled stoichiometry. Our synthetic chemistry led us to consider $HFe_4(CO)_{12}BH_2$ as a potential source of the well known metallic glass $Fe_{80}B_{20}$ (METGLAS)[13], i.e., as illustrated in Scheme 1 $HFe_4(CO)_{12}BH_2$ contains a

$$n \xrightarrow{\Delta} 12n \; CO\uparrow + \; 3n/2 \; H_2\uparrow + \left[\right]_n$$
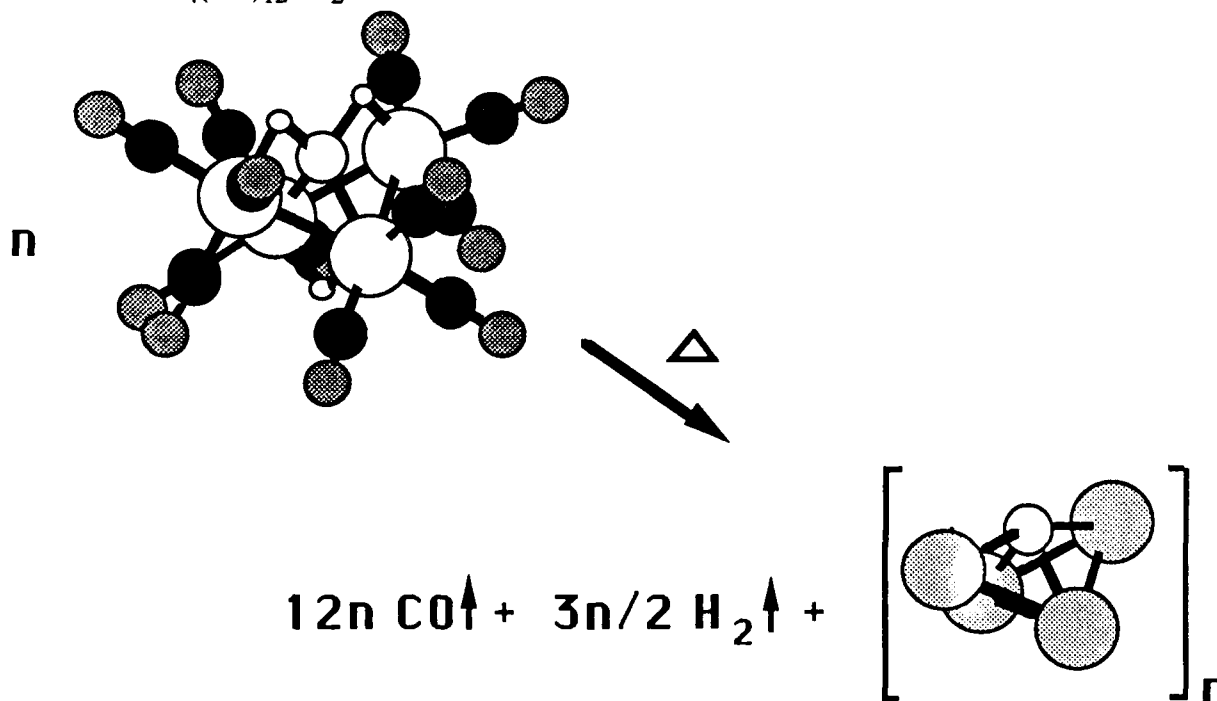
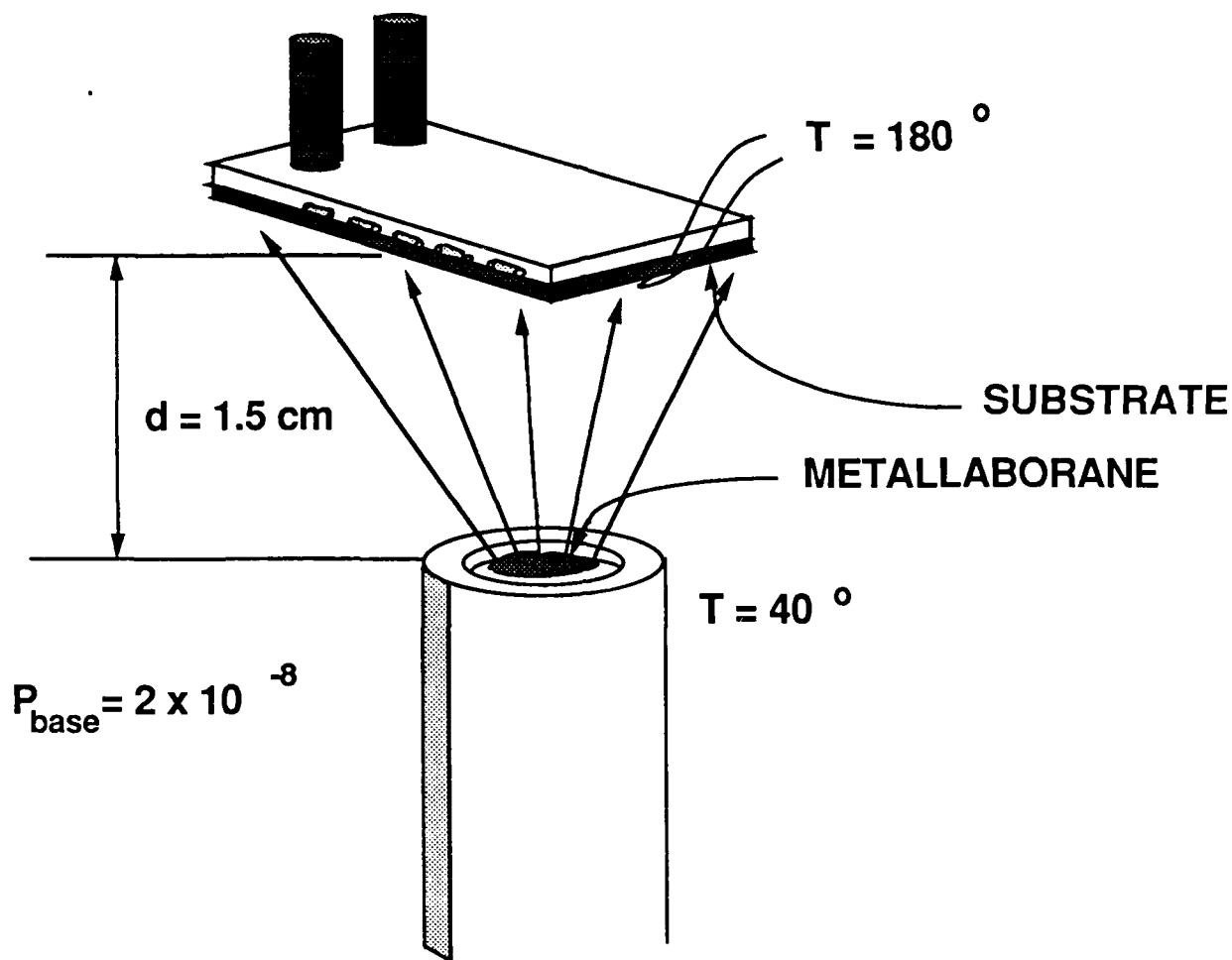**Scheme 1**

possible building block of the $Fe_{80}B_{20}$ material coordinated to CO and H ligands[14]. This compound was an ideal starting point as the properties of $Fe_{80}B_{20}$ have been thoroughly

defined in the literature[15]. Hence product characterization was simplified and unusual properties due to the method of preparation, if any, could be easily recognized.

Preliminary experiments showed that $HFe_4(CO)_{12}BH_2$ decomposed under thermolytic conditions to yield CO and H_2 plus a residual solid containing boron and iron. Films were prepared by subliming $HFe_4(CO)_{12}BH_2$ in a low pressure (base pressure 10^{-8} torr, deposition pressure 10^{-4} torr) MOCVD reactor of our own design (Scheme 2) on substrates resistively heated to 180°C. Uniform, contiguous films of 1000Å in thickness with a metallic luster were grown in ca 30 m on glass, silicon and metal substrates. The films adhere well to all substrates examined and were amorphous to X-rays. Analysis by Auger and XPS showed a Fe : B ratio of 4 : 1 and no impurities other than carbon and oxygen (< 5%). The chemical environment of the boron atom as measured by the 1s binding energy is identical to that of the authentic material. Mössbauer spectroscopy reveals a material with an isomer shift, quadrupole splitting and hyperfine fields typical of the authentic amorphous metal. Resistivity measurements (four point method) yield values two times larger than those of those of the bulk materials. These results unambiguously define $HFe_4(CO)_{12}BH_2$ as a useful single precursor for the production of thin films of an authentic metallic glass under mild conditions. A preliminary report of our work has appeared[16].

When these studies were initiated it was not clear that loss of 12 CO ligands and 3 H atoms from $HFe_4(CO)_{12}BH_2$ would be rapid with respect to film build up. In addition, we realized that carbide formation by loss of CO_2 might well be competitive with CO loss. Indeed this is a known route to carbido clusters[17]. In the event neither of these factors caused problems. At temperatures below 200°C complete ligand loss is observed and it is only at temperatures above 250°C that carbide formation takes place. However, an unanticipated problem added complexity to an apparently simple deposition process. Although oxidation of $Fe_{80}B_{20}$ has been observed[18], during deposition the boron atoms in these metal-rich borides are extremely reactive to oxygen sources. For example, in an oxygen free boride film, the reactivity of the boron atom is high enough that one can watch the oxidized boron peak increase substantially at the expense of the boride peak (2x in ca 30 m) after ion milling even in the clean environment of the Auger spectrometer (Scheme 3). Hence, the production of the iron-boride films described above requires
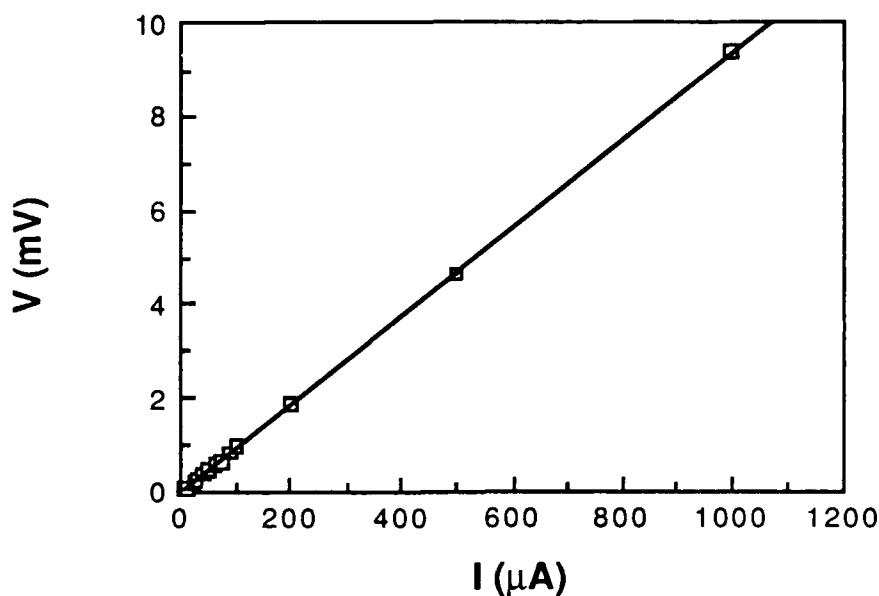
Scheme 2

a very clean environment. Deposition in our initial apparatus under normal MOCVD conditions (base pressure 10^{-6} torr) leads to films with high oxygen contents, e.g., 30%, and with a large fraction of the boron in an oxidized form as judged by XPS. The films are dark in color, resistivities are high and the Mössbauer spectra show a doublet besides the six-line spectrum of $Fe_{80}B_{20}$ indicating the presence of another type of iron environment. It was only by constructing a deposition system that operated at a base pressure of 10^{-8} torr that we were able to produce films with oxygen levels below 5%. Except for the surface of the film which contains a high oxygen level the bulk material once deposited does not oxidize in air. Although the high reactivity of these boron centers in a highly metallic environment created a problem in producing a pure film, we suggest below that it may constitute a useful feature for the development of selectively oxidized materials.
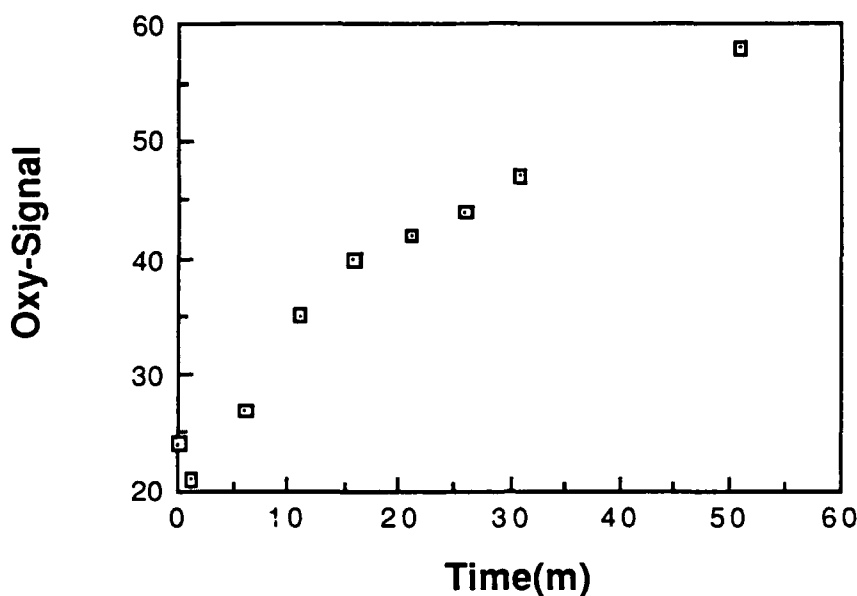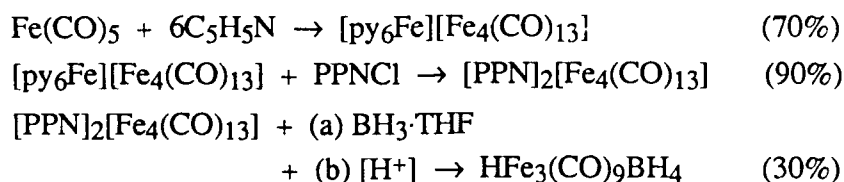
Scheme 3

We have also explored the use of $HFe_3(CO)_9BH_4$[19] as a precursor to the known $Fe_{75}B_{25}$ system. Because of the somewhat higher vapor pressure of the solid, film formation is even more facile than in the tetrairon system. Uniform, smooth ($\pm 50Å$) films ranging in thickness from 1000 to 10,000 Å can be grown in 30-60 m depending on the source-substrate configuration. Again the films are amorphous and the stoichiometry of the cluster core is transferred intact to the solid film. Purities, as determined by Auger spectroscopy, are somewhat higher than those from the four-iron cluster. Low system base pressures are still required to produce films with no oxidized boron. These films also exhibit Ohmic behavior (Scheme 4) and resistivities only 40% higher than the bulk material are measured. This confirms the high purity of the films and indicates low porosity and/or low densities of other defects in the films.

As both of these metallaborane clusters are stable, only slightly air sensitive materials, and have low but useable vapor pressures at room temperature, they constitute convenient precursors for the deposition of $Fe_{80}B_{20}$ and $Fe_{75}B_{25}$ films at low temperatures on a variety of substrates. Of course the availability of the metallaborane clusters is also important. Our published preparative routes to $HFe_3(CO)_9BH_4$ and $HFe_4(CO)_{12}BH_2$ are neither straightforward nor of high yield. Hence we have devoted a significant amount of time to the development of more practical routes to these two cluster systems with some
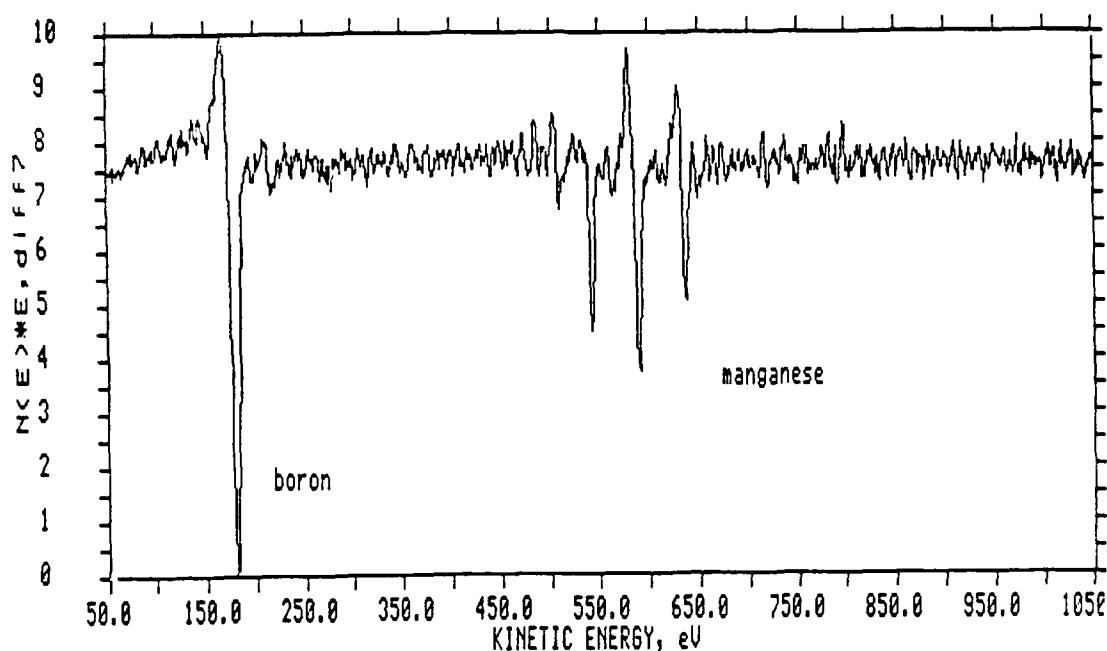
Scheme 4

success. For example, from three reaction steps, the first two of which are literature reactions:

$$Fe(CO)_5 + 6C_5H_5N \rightarrow [py_6Fe][Fe_4(CO)_{13}] \qquad (70\%)$$

$$[py_6Fe][Fe_4(CO)_{13}] + PPNCl \rightarrow [PPN]_2[Fe_4(CO)_{13}] \qquad (90\%)$$

$$[PPN]_2[Fe_4(CO)_{13}] + (a) BH_3 \cdot THF$$
$$+ (b) [H^+] \rightarrow HFe_3(CO)_9BH_4 \qquad (30\%)$$

followed by filtration through silica gel and fractional crystallization, we can isolate pure $HFe_3(CO)_9BH_4$ in 30% yield as a free flowing dark red-orange solid that can be used directly for deposition[20]. Note that the starting materials are all readily available and, with the exception of the borane and PPNCl are inexpensive. We have already demonstrated the quantitative conversion of $HFe_3(CO)_9BH_4$ into $HFe_4(CO)_{12}BH_2$ by treatment with $Fe_2(CO)_9$[21]. and have developed equally good routes to related ferraboranes.

2. Transition Metal Borides: As metal-rich borides with isolated boron atoms constitute only a small fraction of known binary transition metal borides[22], our secondary objective was to explore boron-rich metallaboranes. Recently two accounts of the utilization of metal borohydrides for the production of refractory borides have appeared[3,6]. Our initial work, in collaboration with Gaines at Wisconsin, has been carried

out on $B_5H_{10}Mn(CO)_3$ which is a volatile liquid metallaborane that can be prepared in good yield in a metal catalyzed reaction from B_5H_9, H_2, and $Mn_2(CO)_{10}$[23]. Deposition in either high (10^{-8} torr) or low (10^{-5} torr) vacuum systems at 350°C leads to films having the stoichiometry MnB_4 with very low carbon and oxygen levels ($< 2\%$, Scheme 5). Films are dark and metallic in appearance and grow to a thickness

Scheme 5

of 5000 to 10,000Å in 30 m depending on metallaborane pressure. The films produced at low pressure have better appearances, lower resistivities and adhere more strongly to a glass substrate. The observed stoichiometry suggests that not only are CO and H_2 produced on thermal decomposition but B_2H_6 is as well. In contrast to the metal-rich systems the film shows no tendency for oxidation under conditions of Auger analysis (10^{-8} torr with argon ion gun in operation). There is a known crystalline boride of composition MnB_4 but the films of the refractory substance with the same composition produced from $B_5H_{10}Mn(CO)_3$ at low temperatures are amorphous by X-ray[24]. Measured resistivities are higher than those of the metal-rich systems and related, known crystalline manganese borides. We have yet to fully define the source of these differences but it is quite possible that they originate in the fact that the material produced at relatively low temperatures has a significantly different structure which may give rise to different properties. These results are being communicated[25].

3. Other Metal-Main Group Precursors: Our final objective was to extend this approach to metal-rich clusters containing main group elements other than boron in the cluster framework. To this end we have examined the deposition behavior of $HFe_4(CO)_{12}N$[26] and $HFe_4(CO)_{12}CH$[27]. Both of these clusters are isoelectronic and essentially isostructural with $HFe_4(CO)_{12}BH_2$ and their behavior under thermal deposition conditions was expected to provide a chemically interesting contrast to that of the metallaborane. Under essentially the same conditions used for the ferraborane, the carbon and nitrogen analogues yield highly specular films that adhere well to glass and metal substrates. Much less susceptability to oxidation is observed and oxygen free films ($< 4\%$) can be obtained with typical MOCVD base pressures of 10^{-6} torr. In the case of the carbide the Fe : C ratio is 4 : 1 and the film is amorphous. However, in the case of the nitride the Fe : N ration is ≈ 8 : 1 and an αFe crystalline phase is observed by X-ray diffraction. In the nitride film Mössbauer spectroscopy shows the presence of two types of iron in a ratio of about 1 : 1 and one of the sextets corresponds to that of αFe (Scheme 6). The other sextet is similar to one
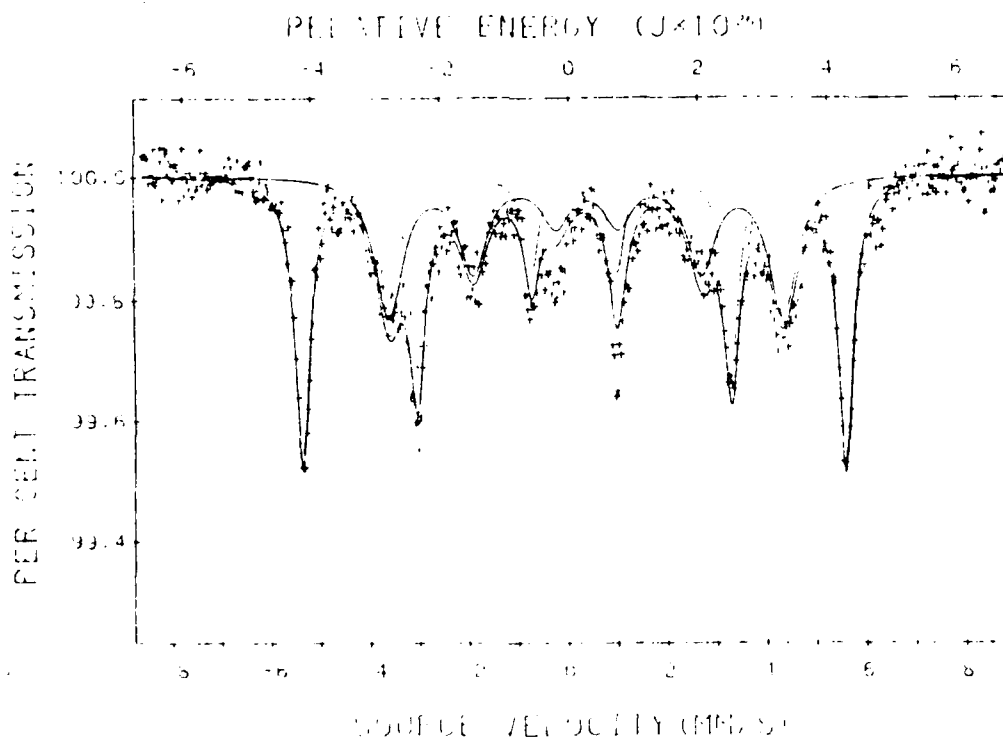
Scheme 6

of several observed for an iron-nitride phase having the composition Fe_4N[28]. Clearly the decomposition of $HFe_4(CO)_{12}N$ on a glass substrate involves not only CO and H_2 loss but also a pathway whereby nitrogen is lost. These results are being communicated[29].

Summary: Our work has demonstrated that the cores of molecular transition ʳ .ɔtal clusters containing main group atoms constitute building blocks for solid state thin films. These building blocks can be released under mild conditions to yield pure materials with good properties on a variety of substrates. There is a direct, although not necessarily simple, chemical relationship between cluster stoichiometry and cluster core composition. As there are a substantial number of metallaboranes known, this work establishes them as potential sources for the production of alloy and refractory thin films of metal borides under mild conditions. In addition, the results suggest that the approach need not be restricted to metallaboranes but that metal-main group atom clusters in general constitute new, low temperature sources of a variety of alloy phases in thin film form.

Collaborations: It is important to note that this work has involved productive collaborations with a number of other scientists. I particularly acknowledge collaborations with W. F. Stickle (Perkin-Elmer-XPS), G. J. Long and O. A. Pringle (Univ. Missouri-Rolla-Mössbauer), F. P. Fehlner (Corning Glass-SIMS), W. Pietro (Wisconsin-Resistivities), and D. F. Gaines (Univ. Wisconsin-MnB_4) as well as my interactions with members of the Thin Film Institute of the University of Wisconsin during a sabbatical leave in the 1988-89 academic year.

C. LIST OF ALL PUBLICATIONS

1. "Alloy Thin Films from Discrete Metallaborane Clusters", T. P. Fehlner, M. M. Amini, M. V. Zeller, W. F. Stickle, O. A. Pringle, G. J. Long and F. P. Fehlner, Mat. Res. Soc. Symp. Proc. 131, 413 (1989).

2. "A New Technique for the Nitridation of Iron. Preparation an Iron-Nitride Film from a Molecular Tetrairon Nitrido Cluster", T. P. Fehlner, M. M. Amini, W. F. Stickle, O. A. Pringle, G. J. Long and F. P. Fehlner, Chemistry of Materials, submitted, 18 Sept. 89.

3. "Metallaboranes as Molecular Precursors to Thin Metal-Boride Films. The Conversion of $HFe_3(CO)_9BH_4$ to Amorphous $Fe_{75}B_{25}$", M. M. Amini, T. P. Fehlner, G. J. Long and M. Politowski, J. Am. Chem. Soc., submitted 20 Nov 89.

4. "Synthesis and Characterization of $(CO)_4FeSe_2$. A Useful Precursor to $(CO)_6Fe_2B_2H_6$", X. Meng and T. P. Fehlner, to be submitted ca Jan 90.

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2. Xiangsheng Meng, Ph.D. expected January 1990

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